NOVEL MAGNETISM IN PERMANENT MAGNETS

R. Grössinger
Institute F. Festkörperphysik, TU Wien
Wiedner Hauptstrasse 8-10, A-1040 Vienna, Austria

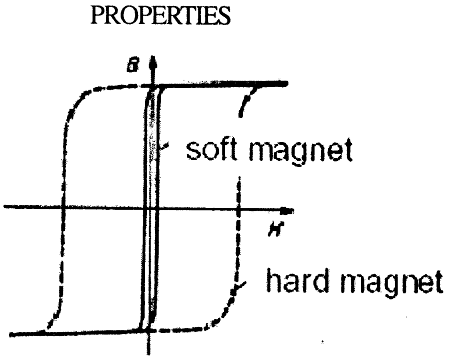
ABSTRACT

An overview on the physics of hard magnetic materials is given. The basic considerations leading to hard magnetic properties are discussed. All groups of industrial permanent magnets such as: Al-Ni-Co, ferrites, Sm-Co based, Nd-Fe-B are presented. The most important production methods are described. The advantage and disadvantages of each magnet group is given.

Key words : Hard-magnetic materials, magnetic properties, micro-structure

INTRODUCTION

Magnetic ordered materials are generally characterized by the hysteresis loop, where the magnetization M is measured as a function of the magnetic field H – see Figure 1. The magnitude of the coercivity H_C determines if the material is called magnetically soft (low coercivity 1 A/m < H_C < 100 A/m) or magnetically hard (H_C between 80 kA/m and 1600 kA/m). Generally there is a huge demand on the world market (about 30 B$) concerning magnetic materials as shown in Figure 2 [1]. Therefore many groups in the whole world make big effort to develop and improve magnetic materials for various applications.



Figute 1. Typical hysteresis loop of a magnetically ordered material.

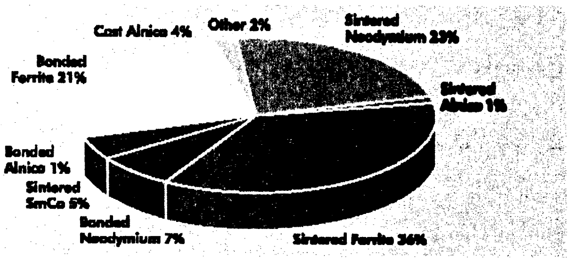


Figure 2. World market of magnetic materials.

The development of hard magnetic materials started already with the discovery of Fe-C steels. In the last century the technical performance was dramatically improved. A key number for permanent magnets is the energy density (described by kJ/m^3) stored in the optimum working point of a magnetic material – see also Figure 6. Figure 3 shows the improvement of the stored energy density $(B.H)_{max}$ achieved within the last hundred years. One can see that an improvement of more than a factor 10 was achieved. This was mainly possible by a huge increase of the coercivity. The enlargement of the coercivity became possible by the discovery of materials with a high magnetocrystaline anisotropy such as the rare-earth-3d intermetallics.

In order to understand the energy density product better I refer to Table I where a comparison between different energy storing systems is given. Concerning gasoline a permanent magnet is a low energy storage system, compared with a standard Pb accumulator the stored energy density is rather high.

So all these data indicate the importance and significance of permanent magnet materials. In the following a survey about the basic concept as well as the magnetic properties of the different magnet families will be given.

Table 1. Comparison of energy storing systems

Gasoline	44 000 kJ/kg
Falling water (Az = 100m)	980 kJ/kg
Pb-acid battery	119 kJ/kg
Best Magnet	440 kJ/kg

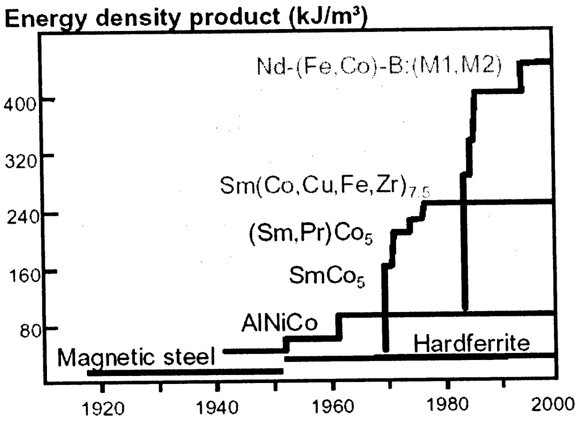


Figure 3. Improvement of the energy density product within the last hundred years.

Fundamental Properties

One has to distinguish between intrinsic and extrinsic properties which are important for a high quality permanent magnet. The intrinsic properties combined with the actual microstructure (grain size and shapes, phases, structures etc.) determine the extrinsic properties.

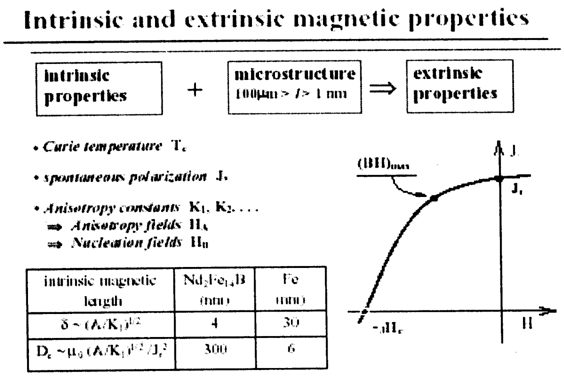
The following intrinsic properties are important for permanent magnets:

1. High saturation magnetization at room temperature – therefore the 3d-metals such as Fe or Co are used. A high saturation magnetization is also necessary to achieve a high energy product
2. High Curie-temperature T_C; here again the 3d metals are necessary, because the direct exchange between the 3d electrons causes a high ordering temperature. A high T_C value is needed for all industrial applications.
3. High anisotropy; the use of 4f metals is favourable because they exhibit generally an orbital moment ***L*** which causes a high magnetocrystalline anisotropy. The anisotropy can be described either by the so-called anisotropy field H_A or by the anisotropy constants K_1, K_2, K_3..... The anisotropy constants determine generally the nucleation field which is an important parameter for the mobility of the domains and consequently for the magnetization process. The condition of a high uniaxial anisotropy is necessary for achieving a high coercivity.

The following extrinsic properties are important for permanent magnets:

1. High energy product $(B.H)_{max}$, which scales with B_r^2 – therefore a high saturation magnetization determines together with the degree of alignment the maximum possible stored energy. For isotropic, uniaxial material is $B_r = B_S/2$ – therefore is $(B.H)_{max}$ in an isotropic material principally much smaller! Generally is a large energy density very important for application with a high degree of miniaturisation!
2. High coercivity – beside the magnetocrystalline anisotropy a well adjusted microstructure determines mainly the coercivity.
3. Thermal stability – this is given by the temperature dependence of the magnetization of all involved phases.
4. Mechanical properties – here again the microstrucure plays a leading role.
5. Corrosion stable – this depends on the chemical composition of the involved phases as well as on the microstructure.

The interplay between intrinsic and extrinsic properties is shown in Figure 4 [2].



intrinsic magnetic length	$Nd_2Fe_{14}B$ (nm)	Fe (nm)
$\delta \sim (A/K_1)^{1/2}$	4	30
$D_c \sim \mu_0 (A/K_1)^{1/2}/J_s^2$	300	6

Figure 4. Relation between intrinsic and extrinsic magnetic properties determining a hard magnetic material.

Figure 5 shows also as a comparison the difference between the M(H) and the B(H) loop which is based on the fundamental equation: $B = \mu_0(H+M)$. Additionally the working point and consequently the determination of the energy product $(B.H)_{max}$ is demonstrated. The virgin curve as well as minor loops are important for analysing the coercivity mechanism as well as for hysteresis modelling.

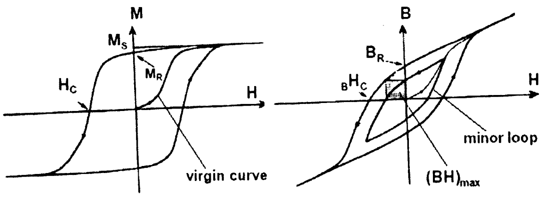


Figure 5. Hysteresis loops for a permanent magnet: (left) M-H loop and (right) B-H loop. The initial magnetization curve after thermal demagnetization starts at the origin, a minor loop arising after the application of fields insufficient for saturation is also shown. The energy product $(BH)_{max}$ is the shaded area in the second quadrant of the B-H loop.

Figure 6 shows the demagnetising curve B(H) in the second quadrant for different hard magnetic materials. It also demonstrates how the working point is found. The arrow indicates a working point, which is given by the geometry of the sample (the slope is reciprocal proportional to the demagnetising factor) [3].

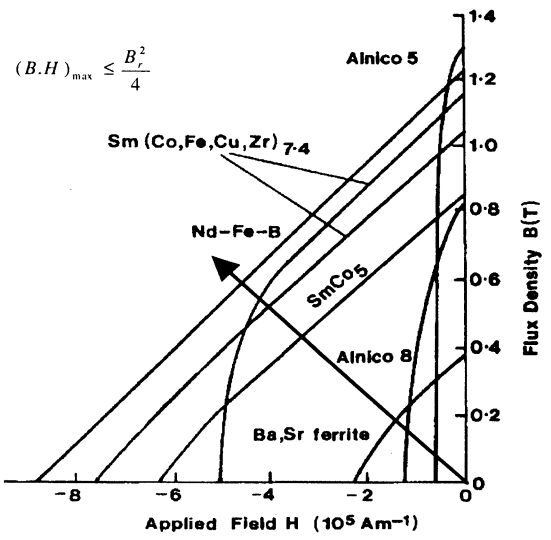


Figure 6. Demagnetizing curve in the second quadrant for different permanent magnets.

Basic Principles

As mentioned already play the 3d-metals such as Fe or Co an important role for magnetic materials the reason is that these materials exhibit the highest saturation magnetization at room temperature. Especially alloys between Fe and Co exhibit the highest possible saturation magnetization which is about 2.5 μ_B/atom. This behaviour is demonstrated in Figure 7 where already Slater-Pauling showed that the magnetic moment as a function of the numbers of the outer electrons exhibiting a maximum between Fe-Co. This behaviour was also found for many other mixed crystal systems where Fe and Co where substituted.

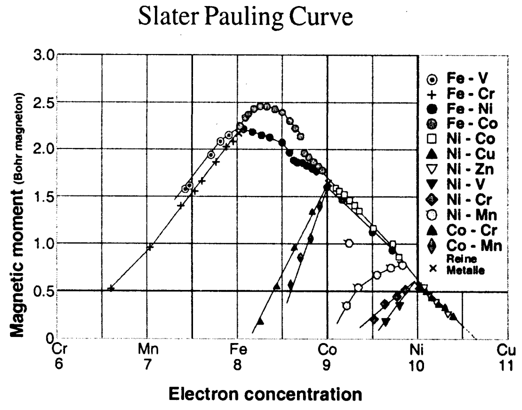


Figure 7. Remanence versus coercivity field for the different permanent magnet materials [3]. Slater-Pauling curve: magnetic moment as a function of the numbers of the outer electrons for different alloys.

As mentioned already for achieving a high coercivity a high anisotropy is necessary. In Alnico the coercivity is based on the shape anisotropy of Fe-Co-needles. The hard magnetic M-type ferrites where the first magnet family where the uniaxial magnetocrystalline anisotropy causes a high coercivity. This is demonstrated by measuring the hysteresis loop on a ferrite parallel and perpendicular to the preferential axis, as shown in Figure 8. Later at the rare earth based magnets the huge anisotropy of compounds such as $SmCo_5$, Sm_2Co_{17} or $Nd2Fe_{14}B$ caused a drastic increase of the achievable coercivity. After this short introduction the properties of the different technical permanent magnets will be surveyed.

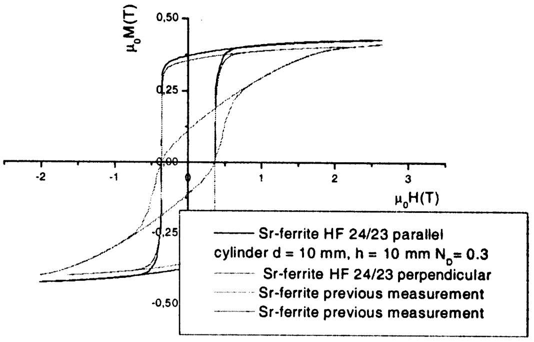


Figure 8. Room temperature hysteresis loop on a Sr-ferrite measured parallel and perpendicular to the preferential axis.

THE PERMANENT MAGNET FAMILIES

There are five important industrial magnet families:

a) AlNiCo
b) Ferrite
c) Sm-Co magnets – based on 1/5.
d) Sm-Co magnets based on 2/17.
e) Nd-Fe-B magnets.

In Table 2 the properties of these three permanent magnet families are shown. The relative prices are normalised to that of a sintered Sm-Co magnet (100%) – see first raw. The last raw show that all kind of plastic bonded material is superior with respect of machinability, however these materials exhibit a lower working temperature and naturally a lower energy density.

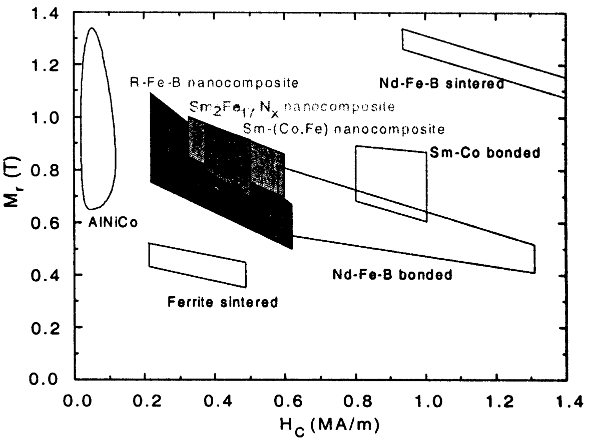


Figure 9. Remanence versus coercivity field for the different permanent magnet materials [3].

Table 2. Permanent Magnet Material Comparison Table

Material	Cost Index	Maximum Energy Products (BH)max (MGOe)	Coercivity $_iH_c$ (kOe)	Maximum Working Temperature (°C)	Machinability
Nd-Fe-B (sintered)	65%	Up to 45	Up to 30	130	Fair
Nd-Fe-B (bonded)	50%	Up to 10	Up to 11	100	Good
Sm-Co (sintered)	100%	Up to 30	Up to 50	300	Difficult
Sm-Co (bonded)	85%	Up to 12	Up to 10	120	Fair
Alnico	30%	Up to 10	Up to 2	550	Difficult
Hard Ferrite	5%	Up to 4	Up to 3	300	Fair
Flexible	2%	Up to 2	Up to 3	100	Excellent
Note: The data listed in table are for reference only					

In Figure 9 the remanence M_r of various permanent magnet materials is plotted versus the coercivity. One can see very clear that the sintered Nd-Fe-B based materials exhibit the highest values of remanence and coercivity.

Production Route of Permanent Magnets

Permanent magnet materials consist usually of different phases which have to be brought (milled, sintered etc.) together in such a way that an "optimal" microstructure is formed. As mentioned already plays here the grain size but also the phase boundary an important role. In order to demonstrate this Figure 10 shows the relation between the coercivity and the mean grain size. The "ideal" permanent magnet consist of magnetically isolated single domain particles.

In order to form such a microstructure the production route has to be considered. Figure 11 gives as a survey the for permanent magnets used production routes. Here a three principally different routes:

a) Sintering
b) Rapidly quenching
c) HDDR (hydrogenation disproportionation desorption recombination)

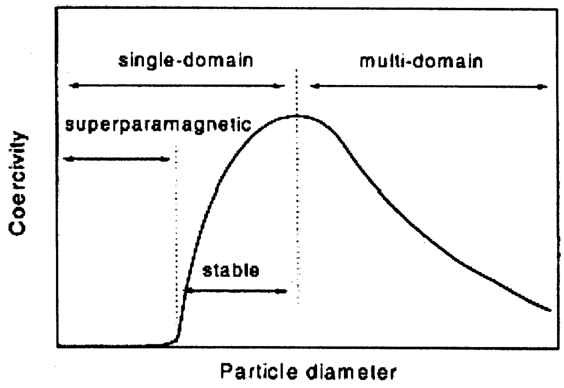


Figure 10. Dependence of the coercivity on the grain size according to [4].

- Melting of the composition
- Grinding of the material
- Pressing together – without or with field
- **Sintering**
- Post – heat treatment

- Melting of the composition
- Producing ribbons by **rapidly quenching**
- Pressing together – at elevated temperatures
- Powder

HDDR

Figure 11. Production routes of permanent magnets

AlNiCo

AlNiCo (Aluminum, Nickel, Cobalt) were introduced by B.J.Arnold in the 1930's [5]. It is characterized by excellent temperature stability, high residual induction, and a high corrosion resistence. These were the first materials specifically designed for permanent magnets to be used in meters and instruments commercially. Their coercivity is based on the shape anisotropy of Fe-Co rich phase. The microstructure of an AlNiComagnet is shown in Figure 12. It is based on a spinoidal decomposition between a weak magnet Fe_2NiAl phase and a needle shaped bcc Fe-Co α-phase, with a high saturation magnetization. Fig. 13 summarises the advantages and disadvantages f this type of magnet.

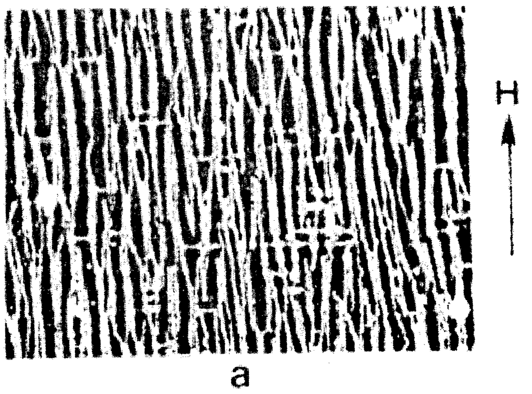


Figure 12. Microstructure of an AlNiCo magnet

Figure 12 Microstructure of an AlNiCo magnet. Figure 13 Advantages and disadvantages of AlNiCo magnets.

Positive Properties
High Corrosion Resistance
High Mechanical Strength
High Temperature Stability
Low Costs

Negative Properties
Low Coercive Force
Low Energy Product

Figure 13. Advantages and disadvantages of AlNiCo magnets

Ferrites

Induced by their favourite performance/price ratio, ceramic anisotropic ferrite magnets are located in the centre of the permanent magnet market, where requirements with respect to performance and/or allowable magnet volume are serious, but not extreme. The main application for high grade ferrite magnets is as segments for various DC motors for the automotive industry.

The evolution of the technology has proceeded in three more or less distinct steps: a) basic inventions (1952-1960), b) significant improvements (1960-1975) and c) gradual refining of the processing (1975-1995).

a) Although the mineral "Magnetoplumbite" and its structure (M) were known for years, the enormous potentials of the pure $AFe_{12}O_{19}$ (A=Ba,Sr..) compound as commercial magnet material have been generally recognized only in the early fifties. This was induced by its 1st commercial introduction under the trade name FERROXDURE (FXD)[6]. A few years later followed two basic technological inventions: wet pressing in a magnetic field to make anisotropic magnets [7] and the use of sinter-aids to promote densification and, in particular, to suppress grain growth during firing [8]. The latter was induced by the notion that high coercivity requires small grain size ($\approx$1um).

b) The 2nd period was characterized by less important, but still significant improvements in the procedure, notably an improved composition (Sr-M), improved sinteraids (Si-based) and the use of Al/Cr substitutions to adjust the $_JH_C/B_r$ ratio. The end of the 2nd period coincides more or less with 25th birthday of FXD, where a 1st review paper was issued [9].

c) In the 3rd period, it became gradually clear that increased magnetic performance asks for decreased milled particle size. This implies increased milling effort and more difficult wet pressing, two factors which largely contribute to the production costs. The magnetic performance (IP) is adjusted by the milled particle size and the Br/HcJ ratio is adjusted by a Al/Cr substitution, where $IP = Br + 0.4\mu_0 {}_JH_C$ (mT), being practically independent of the specific firing and the Al/Cr substitution. For technical and economical reasons, however, there is a lower limit for the milled particle size. The corresponding upper performance level of around IP=550 mT characterizes the saturation state of the classical technology in the early nineties. In this 3rd period, several papers appeared reviewing the science and technology of classical ferrite magnets and its evolution [10-12].

Intrinsic properties: The intrinsic properties stem from the M-crystal structure and ,notably, from the five distinct Fe-sublattices. Two intrinsic properties are crucial: saturation magnetization (J_S) for B_r and anistropy field strength (H_A) for $_JH_C$.

Saturation magnetization (J_S) and its temperature dependence-The five Fe-sublattices are coupled by super-exchange, allowing only parallel (up) or antiparallel (down) orientation. Their mutual orientation is given by the Gorter model [6,9]: 2a(up), 4f1(down), 12k(up), 4f2(down), 2b(up). Taking into account that the magnetic moment for Fe3+ amounts to $5\mu_B$, for the total moment at 0 K is found $20\mu_B$ per mol $AFe_{12}O_{19}$, in agreement with the observed saturation magnetization (J_S). The temperature dependence of J_S is shown in Figure 1, implying J_S(300K) =478 mT. It is remarkable that the J_S-T curve is almost linear in a broad T-region (dJ^oS/dT =-0.9 mT/K). Moessbauer analysis revealed that the latter stems from the 12k-sublattice [4]. Figure 14 shows the structural and magnetic properties (alignement) of the M-type ferrite.

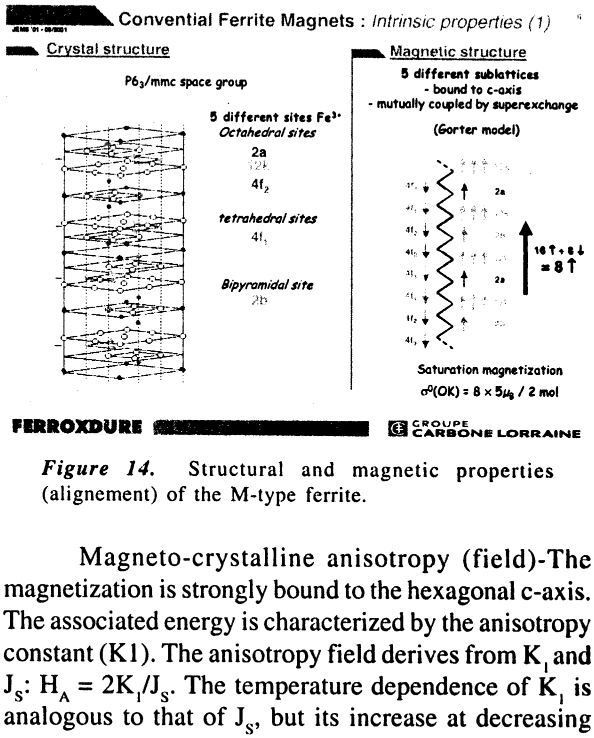
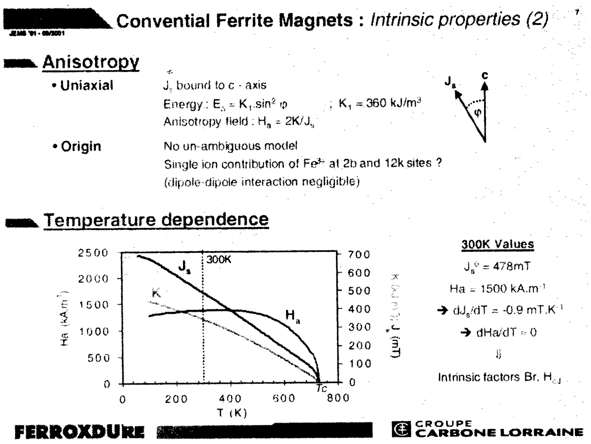


Figure 14. Structural and magnetic properties (alignement) of the M-type ferrite.

Magneto-crystalline anisotropy (field)-The magnetization is strongly bound to the hexagonal c-axis. The associated energy is characterized by the anisotropy constant (K1). The anisotropy field derives from K_1 and J_S: $H_A = 2K_1/J_S$. The temperature dependence of K_1 is analogous to that of J_S, but its increase at decreasing temperature is somewhat less, resulting in a flat H_A-T curve, having a maximum around 300K (Figure 15). There is not yet a clear-cut model for the magneto-crystalline anisotropy. The contribution of dipole-dipole interaction has been calculated to be relatively small. So, the spin-orbit coupling of the Fe3+ ions must play the main role, in spite of the fact that (free) Fe3+ has no orbital moment. Mostly, the contribution to the overall spin-orbit coupling is attributed to the 2b site, but the joint 12k sites play also a significant role [9,13]. Figure 15 shows the temperature dependence of the magnetic properties (magnetization, anisotropy) of the M-type ferrite. Figure 16 summarises the advantages and disadvantages of this type of magnet.



Convential Ferrite Magnets : *Intrinsic properties (2)*

Anisotropy

- **Uniaxial** J_s bound to c - axis
  Energy : $E_a = K_1.\sin^2\varphi$; $K_1 = 360\ kJ/m^3$
  Anisotropy field : $H_a = 2K/J_s$
- **Origin** No un-ambiguous model
  Single ion contribution of Fe^{3+} at 2b and 12k sites ?
  (dipole-dipole interaction negligible)

Temperature dependence

300K Values

$J_s^0 = 478mT$
$Ha = 1500\ kA.m^{-1}$
→ $dJ_s/dT = -0.9\ mT.K^{-1}$
→ $dHa/dT \approx 0$
⇓
Intrinsic factors Br, H_{cJ}

Figure 15. Temperature dependence of the magnetic properties (magnetization, anisotropy) of the M-type ferrite.

Ferrites

Positive
Low Cost
High Coercive Force
High Resistance to Corrosion

Negative
Low Energy Product
Low Mechanical Strength - Brittle

Figure 16. Advantages and disadvantages of ferrite magnet.

HISTORY OF RARE-EARTH MAGNETS

Rare earth cobalt magnets became commercially available in the late 1960's. They offered a significant jump in magnetic energy from the Alnico and ferrite magnets then available. Energy products for Samarium Cobalt range from 16 to 32 MGOe. The most common rare earth element used in this group of materials is samarium. Samarium cobalt (Sm-Co) magnets are produced by pressing powdered alloys to shape and then sintering them in a furnace. This powder can also be mixed with polymer binders to form bonded magnets. Sm-Co exhibits excellent thermal characteristics with several grades designed specifically for applications up to 300°C. For high-energy material, Sm-Co offers the best resistance to temperature effects.

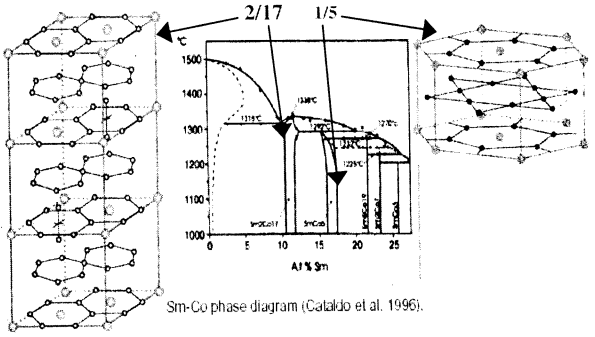
Rare earth iron boron magnets became commercially available in the mid 1980's and have grown increasingly popular ever since. The most commonly produced material is neodymium iron boron (Nd-Fe-B). This group of magnetic materials provides the highest available magnetic energies of any material, ranging from 26 to 48 MGOe. This material can be formed by either pressing and sintering the powder or by bonding with plastic binders. Sintered Nd-Fe-B parts however, will produce the highest magnetic properties. Nd-Fe-B is sensitive to heat and should not be used in environments that exceed 150° C. While Nd-Fe-B is less brittle than some other magnetic materials, it should not be used as a structural component in applications. Table 3 summarises the history of rare earth permanent magnets.

Table 3. History of rare earth permanent magnets.

Year	Energy Product	Summary
1966	18 MGOe	Dr. Karl J. Strnat discovers the high energy product of the Samarium-Cobalt (SmCo5) compound.
1972	30 MGOe	Dr. Karl J. Strnat and Dr. Alden Ray develop a higher energy product Samarium-Cobalt (Sm2Co17) compound.
1983	35 MGOe	General Motors, Sumitomo Special Metals and the Chinese Academy of Sciences develop a high energy product Neodymium-Iron-Boron (Nd2Fe14B) compound.

Sm-Co Based Magnets

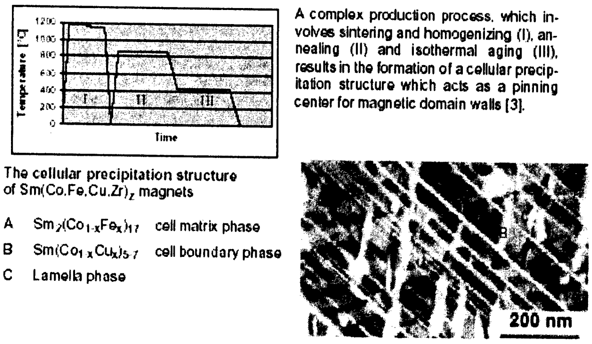
Samarium Cobalt (Sm-Co) magnets offer designers a tremendous combination of extremely high magnetic properties, outstanding thermal stability and excellent corrosion resistance. As part of the rare earth group of permanent magnets, Samarium Cobalt (Sm-Co) magnets typically fall into two families of materials. They include rare earth $SmCo_5$ and Sm_2Co_{17}, and are commonly referred to as 1:5 and 2:17 materials. In Figure 17 the phase diagram of the Sm-Co system is shown. The here important unit cell of each of these structures is also shown.



Sm-Co phase diagram (Cataldo et al. 1996).

Figure 17. Phase diagram of the Sm-Co system together with the unit cells of the 1/5 and 2/17 structure.

In order to achieve the optimum microstructure a well designed heat treatment is very important. Figure 18 shows the temperature versus time profile as well as a microstructure of a Sm-Co based magnet. Figure 19 shows the advantages and disadvantages of Sm-Co based magnets.



A complex production process, which involves sintering and homogenizing (I), annealing (II) and isothermal aging (III), results in the formation of a cellular precipitation structure which acts as a pinning center for magnetic domain walls [3].

The cellular precipitation structure of $Sm(Co,Fe,Cu,Zr)_z$ magnets

A $Sm_2(Co_{1-x}Fe_x)_{17}$ cell matrix phase
B $Sm(Co_{1-x}Cu_x)_{5-7}$ cell boundary phase
C Lamella phase

Figure 18 Temperature versus time profile and microstructure of a Sm-Co based magnet.

Sm-Co based magnets

Positive
High Coercive Force
Medium Corrosion Resistance
High Energy Product
High Temperature Stability

Negative
Low Mechanical Strength - Brittle
High Cost

Figure 19. Advantages and disadvantages of Sm-Co based magnets.

Nd-Fe-B

Nd-Fe-B based magnets were invented now about 20 years ago [see 14, 15]. The excellent hard magnet properties are based on the high saturation polarization of the teatragonal $Nd_2Fe_{14}B$ compound together with the high room temperature anisotropy field (H_A about 70 kOe). Figure 20 shows the tetragonal structure of this material, Figure 21 shows the complex phase diagram of Nd-Fe-B. This third generation of Rare Earth magnets, Neodymium Iron Boron (Nd-Fe-B) magnets are the most powerful and advanced commercialised permanent magnet today. Since they are made from Neodymium, one of the most plentiful rare earth elements, and inexpensive iron, Nd-Fe-B magnets offer the best value in cost and performance.

Nd-Fe-B magnets are available in both sintered and bonded forms. Sintered Nd-Fe-B offers the highest magnetic properties (28 MGOe to 50 MGOe) while Bonded Nd-Fe-B offers lower energy properties however for the advantage of easy machinability. Although bonded magnets do not possess magnetic properties as advanced as those of sintered magnets, they can be made in shapes and sizes that are difficult to achieve with sintering. A variety of coatings can be applied to the magnets' surface to overcome the principle drawback of neodymium-based magnets, their tendency to corrode easily.

$Nd_2Fe_{14}B$, Tetragonal unit cell

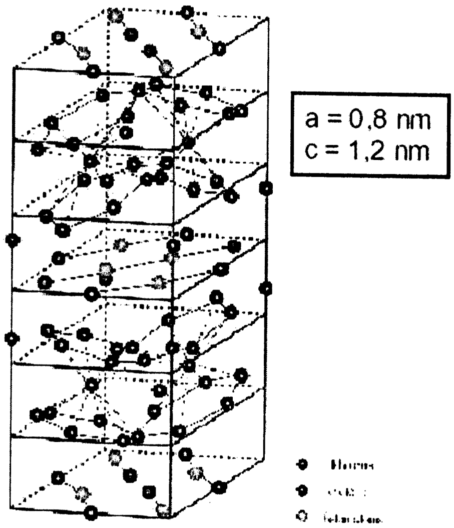
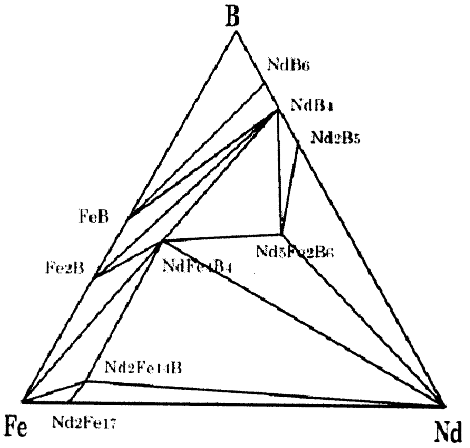


Figure 20. Shows the teatragonal structure of $Nd_2Fe_{14}B$.



isothermal cut at 800°C, after Buschow, Schneider (1986)

Figure 21. Phase diagram of Nd-Fe-B.

In order to demonstrate the excellent properties of this kind of material Figure 22 shows the hysteresis loop as well as the microstructure of a world record Nd-Fe-B based permanent magnet. Figure 23 shows the advantages and disadvantages of Nd-Fe-B based magnets.

SUMMARY

The fundamental ideas which are important for permanent magnets are summarized. The effect of intrinsic

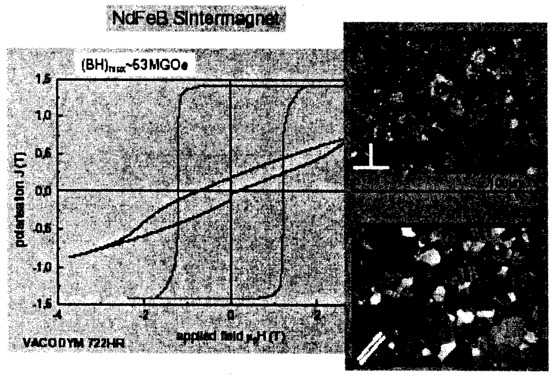


Figure 22. Hysteresis loop as well as the microstructure of a world record Nd-Fe-B based permanent magnet.

Nd-Fe-B magnets

Positive
Very high energy product
High Coercive Force

Negative
High Cost
Low Mechanical Strength – Brittle
Moderate Temperature Stability
Low Corrosion Resistance (uncoated)

Figure 23. Advantages and disadvantages of Nd-Fe-B based magnets.

Table 4. Survey of the physical and thermal properties of the different rare earth magnets.

Physical and Thermal Properties			
Description	SmCo 1-5 Alloys	SmCo 2-17 Alloys	NdFeB
Mechanical Properties:			
Modulus of elasticy	23 x 10^6 psi	17 x 10^6 psi	22 x 10^6 psi
Ultimate tensile strength	6 x 10^3 psi	5 x 10^3 psi	12 x 10^3 psi
Density	8.2 g/cc	8.4 g/cc	7.4 g/cc
Coefficient of thermal expansion:			
Perpendicular to orientation	13 x 10^{-6}/°C	11 x 10^{-6}/°C	-4.8 x 10^{-6}/°C
Parallel to orientation	6 x 10^{-6}/°C	8 x 10^{-6}/°C	3.4 x 10^{-6}/°C
Electrical resistivity	5μ ohm cm	86μ ohm cm	160μ ohm cm
Magnetic Properties:			
Curie temperature	750°C	825°C	310°C
Reversible temperature coefficient of residual induction (-100°C to+100°C)	-0.043%/°C	-0.03% /°C	-0.09 to -0.13% /°C
Recoil permeability	1.05	1.05	1.05
Max. service temperature*	250°C	300°C	150°C

(magnetization, Curie-temperature, anisotropy) and extrinsic properties (coercivity, energy product) is given. The importance of the microstructure for a high coercivity was demonstrated. The magnetic properties of all commercial permanent magnets were described. The advantages and disadvantages of the different magnet families are showen.

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